Effects of Catalyst Hydrophobicity on Rates and Selectivities of Alkene Epoxidation

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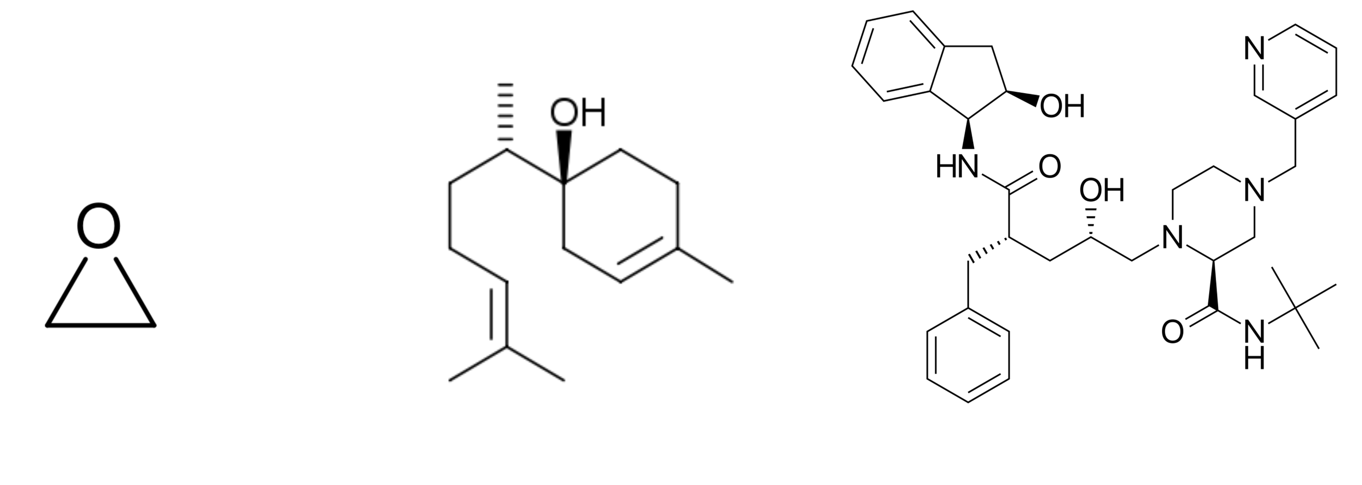
Motivation

- Epoxides are crucial for the production of plastics, fragrances, and pharmaceuticals.[1]

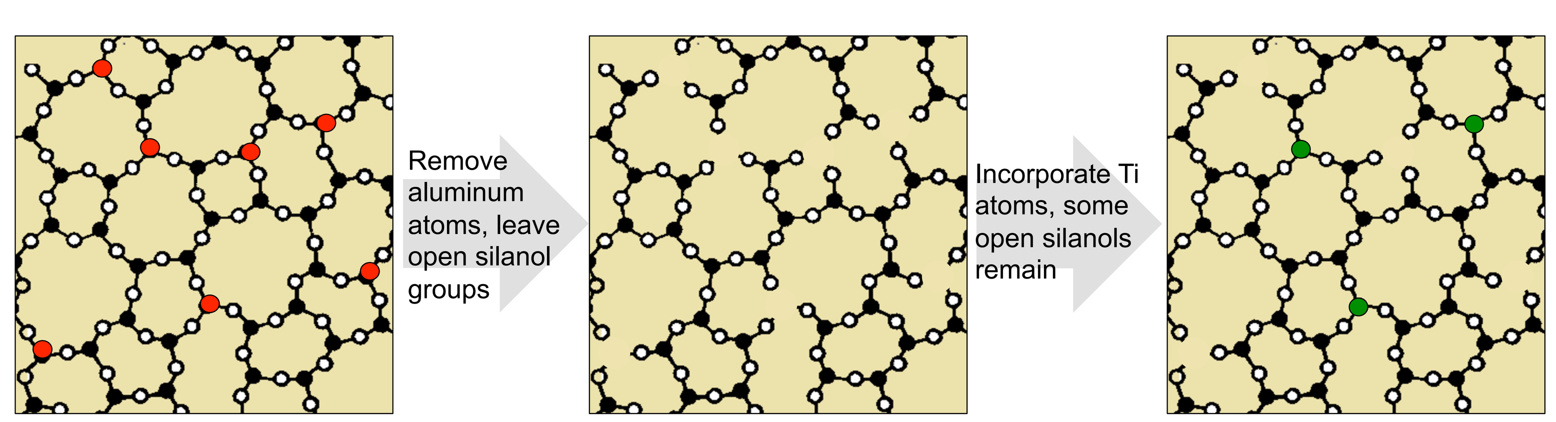


Ethylene oxide: high-value monomer — Bisabolol: floral aroma — Indavinir: HIV/AIDS treatment

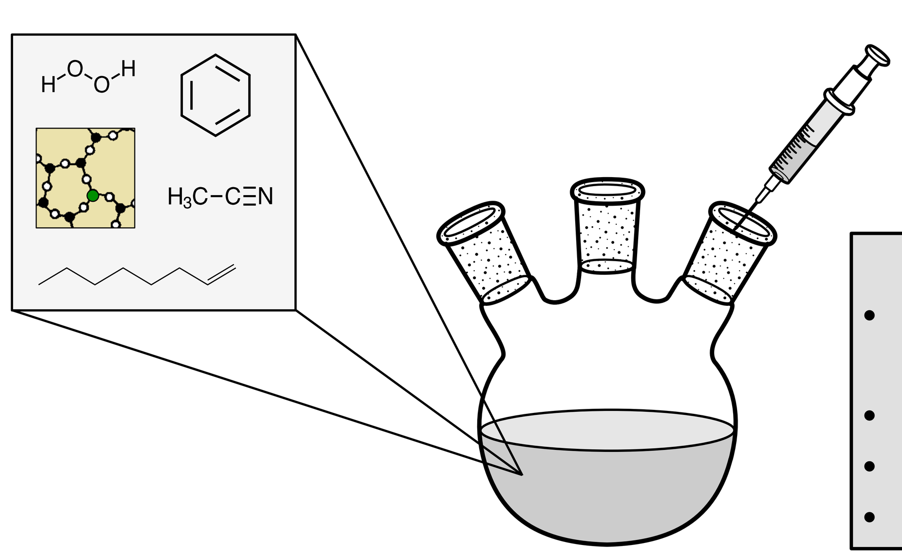
- Current methods of epoxide synthesis require harmful oxidants.[2]
  - emit CO_2
  - produce toxic co-products
- Hydrogen peroxide (H_2O_2) could replace less-green oxidants, but a catalyst is required.
- Hydrophobicity of such catalysts is known to influence their effectiveness.[3]

Materials and Methods

1. Synthesize and characterize catalysts [4]
   - Obtain zeolite samples with various silicon to aluminum ratios
   - Post-synthetically incorporate Ti metal



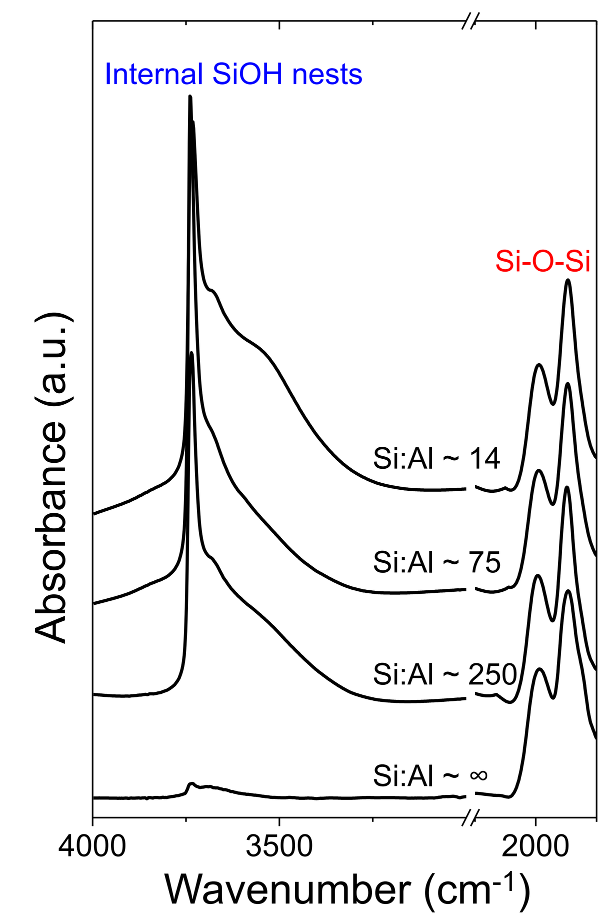
2. Form epoxide



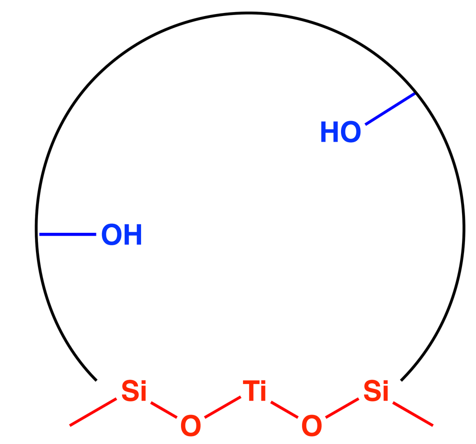
Reaction Conditions
- 0.3 mM 1-octene, 10 mM H_2O_2 in acetonitrile
- 5 μL benzene (internal standard)
- 10-15 mg catalyst
- Heat to 313K

3. Calculate reaction rate and selectivity
   - Remove aliquots over time and analyze with gas chromatograph
   - Determine concentration of species over time, calculate turnover rate

Quantifying Hydrophobicity



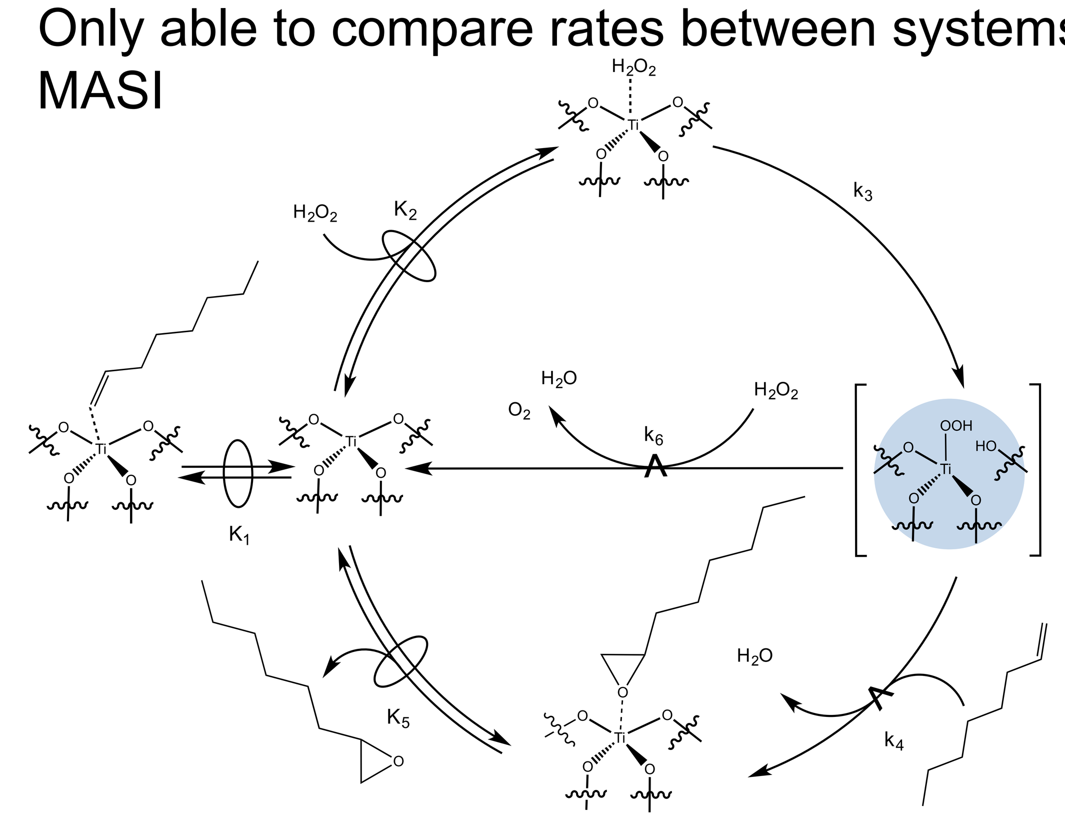
Infrared spectra of dehydrated catalyst samples taken at 50 cm³ min⁻¹ He, 573 K [6]



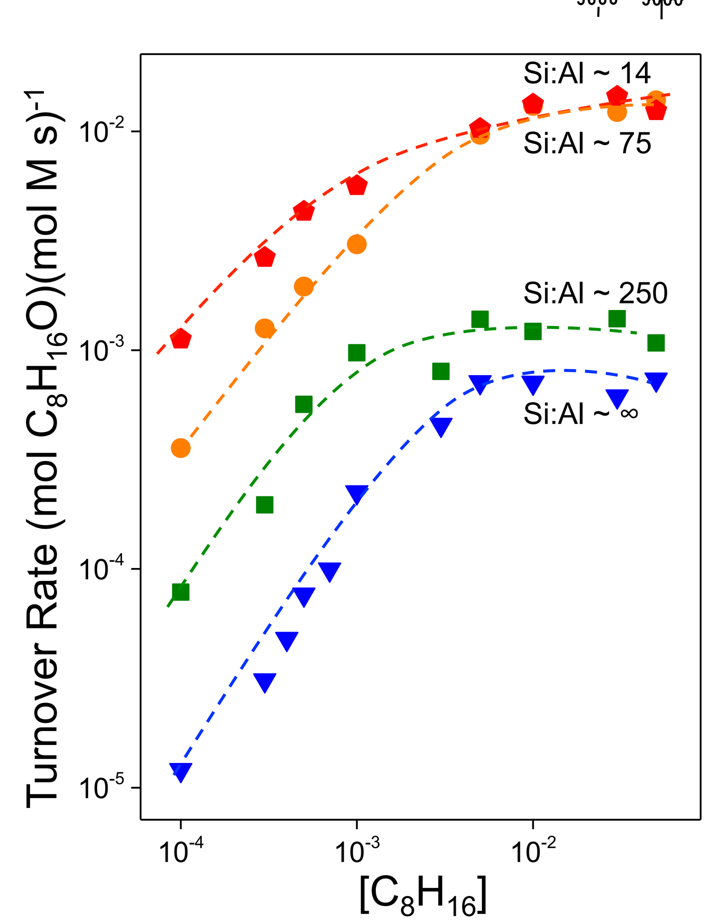
- Silanol density acts as proxy for hydrophobicity
- Measure absorbance peaks for internal silanol nests and Si-O-Si sites
- Define $\varphi = A_{Si\text{-}OH} / A_{Si\text{-}O\text{-}Si}$
- Smaller φ values correspond to more hydrophobic catalysts

Reaction Kinetics and Mechanism

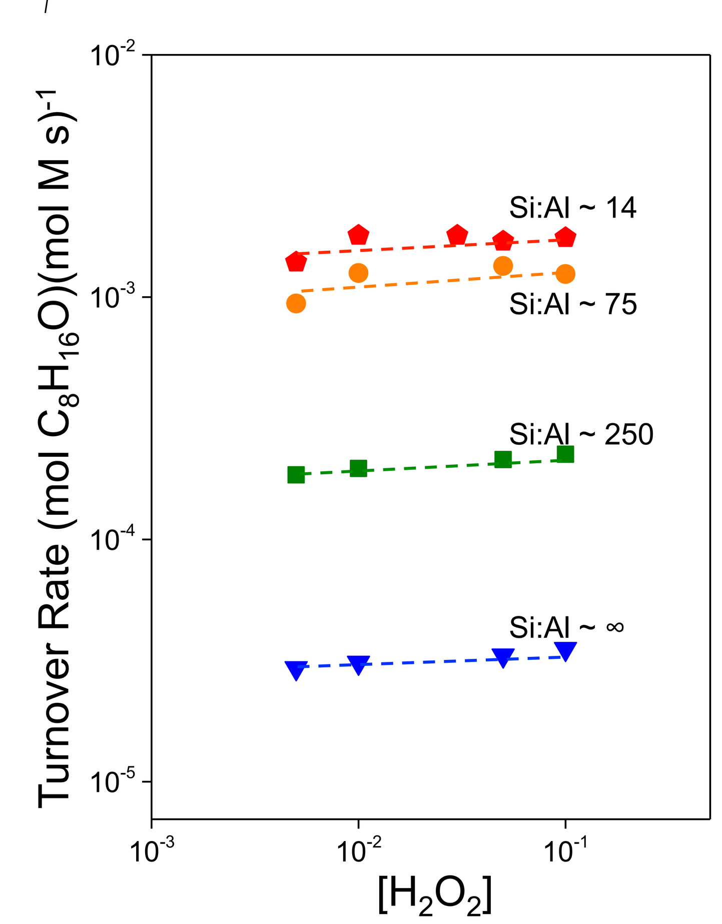
- During reaction, catalyst can be bound to different substrates
- Most abundant surface intermediate (MASI): substrate bound to the most catalytic sites
- Only able to compare rates between systems that have the same MASI



- When $[C_6H_{10}] > [H_2O_2]$, mechanism suggests M-(O_2) MASI and $\frac{r}{[L]} = k_4[C_6H_{10}]^1[H_2O_2]^0$
- Under these conditions, MASI is constant among systems

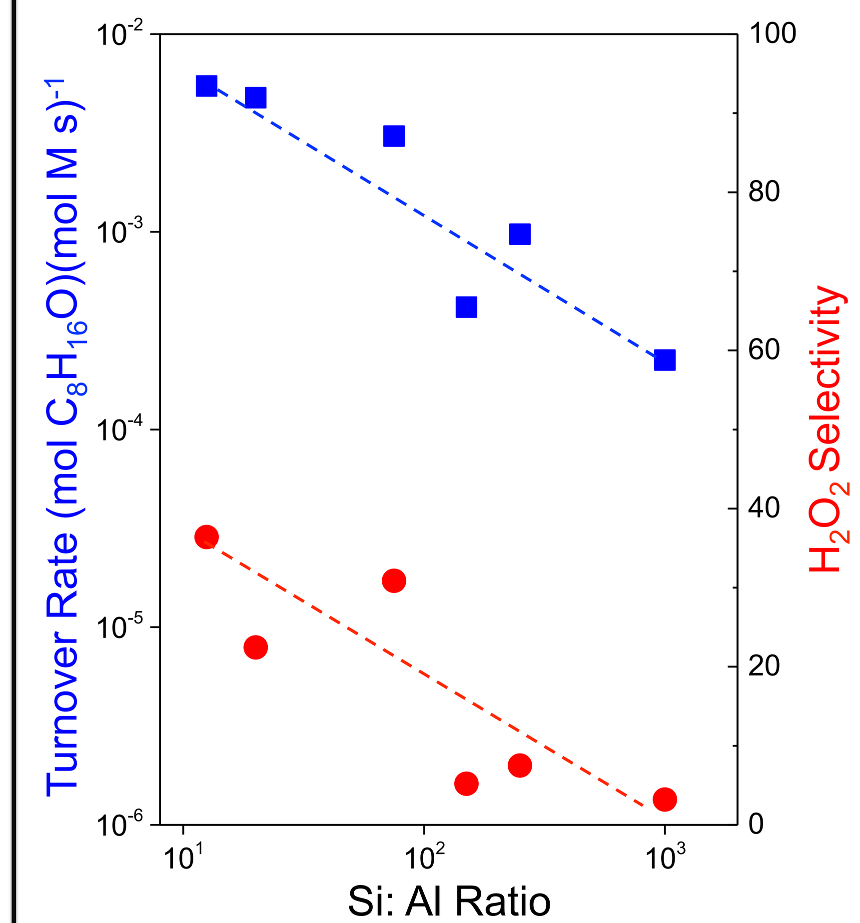


Turnover rate as a function of octene concentration for epoxidation catalyzed by Si:Al~14, 75, 250, and ∞ [6]

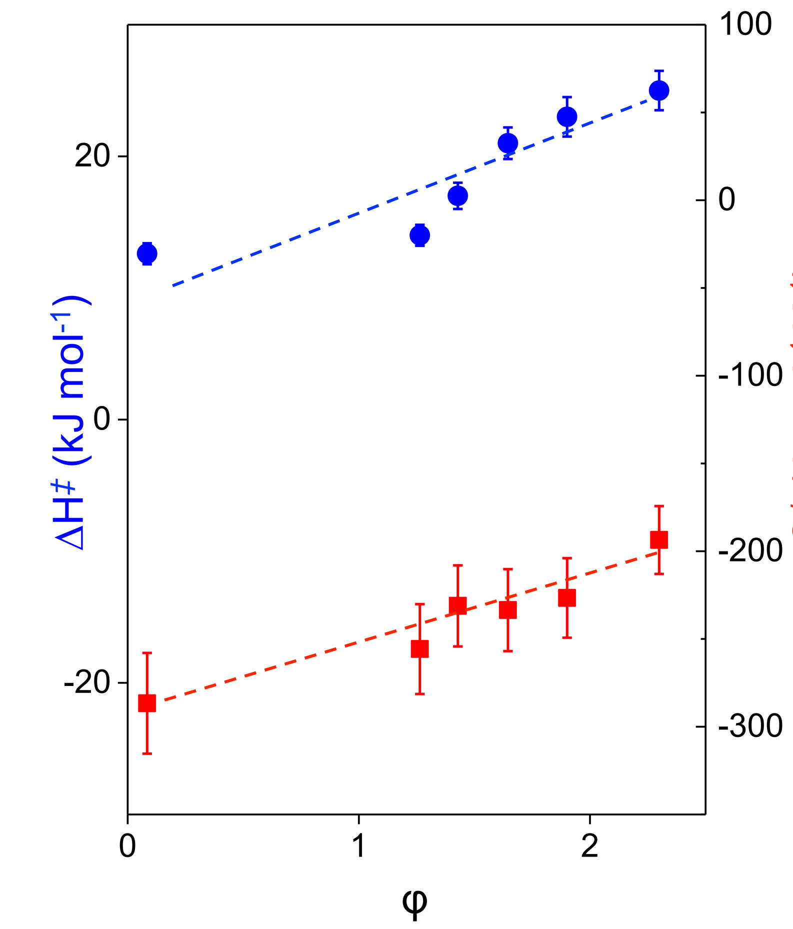


Turnover rate as a function of H_2O_2 concentration for epoxidation catalyzed by Si:Al~14, 75, 250, and ∞ [6]

Rates and Selectivities



Turnover rate and selectivity as a function of silanol density [6]



Reaction barrier and entropic loss as a function of φ [6]

- Increased hydrophobicity lowers reaction barrier but increases entropic loss. Why?
  - Octene (hydrophobic) interacts strongly with hydrophobic catalysts
  - This interaction is enthalpically favorable but entropically costly
- Must balance these two effects

More hydrophobic catalysts correspond to slower reaction rates and poorer selectivity

Conclusions and Future Work

- Reaction conditions found to guarantee constant MASI
- Must balance enthalpy-entropy competition
- Given process conditions, the optimal hydrophobicity can be determined
- Provides design criteria for environmentally-friendly epoxide synthesis
- Explore other factors that may influence catalyst activity

Acknowledgements and References

- Flaherty group
- Frederick Seitz Materials Research Lab

1. Choi, W. J.; Choi, C. Y. *Biotechnol. Bioprocess. Eng.* 10, 167–179.
2. Fyvie, A. *C. Chem. Ind. Lond.* **1964**, 10, 384–388.
3. Harris, S.; Cordon, M. J.; Di Iorio, J. R.; Vega-Villa, J. C.; Ribeiro, F. H.; Gounder, R. *J. Catal.* 2016, 335, 141-154.
4. Dzwigaj, S.; Millot, Y.; Méthivier, C.; Che, M. *Microporous Mesoporous Mater.* **2010**, 130, 162−166.
5. Bregante, D. T.; Flaherty, D. W. *J. Am. Chem. Soc.* **2017**, 130 (20), 6888–6898.
6. Bregante, D. T.; Johnson, A. M.; Patel A. Y.; Flaherty, D. W; J.; *J. Am. Chem. Soc.* To be submitted